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Dual-bed Catalytic System for Direct Conversion of Methane to Liquid Hydrocarbons: Study of Selected Reaction Parameters

N. A. Saidina Amin **Sriraj Ammasi**

Chemical Reaction Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

Tel: 607-5535588; Fax: 607-5581463, Email: noraishah@fkkksa.utm.my

Abstract

A dual-bed catalytic system has been investigated for the direct conversion of methane to liquid hydrocarbons. In this system, methane is converted in the first stage to OCM products over La/MgO catalyst whilst the OCM products are oligomerized to liquid hydrocarbons over Ni loaded HZSM-5 zeolite catalyst. The influence of reaction temperature (650-800 ^{0}C), amount of nickel loading (0-3 wt%) and CH_4/O_2 ratio (4-10) on the process has been studied under atmospheric conditions. The results implied that the Bronsted acid sites of HZSM-5 which acts as an agent for oligomerization would easily be victimized at higher reaction temperature and thus, limits the oligomerization reaction. Oxygen is absolutely necessary for the activation of methane, but it must be kept at favored value in order to suppress the undesirable oxidation reactions. Experimental results also reveal that the unnecessary effect can be minimized by optimizing the amount of nickel loaded on the HZSM-5 catalyst when applied as second bed. This exploration suggests that the concept of dual-bed system is an attractive candidate for methane utilization to produce liquid hydrocarbons.

Keywords: Dual-bed; Methane; HZSM-5; Liquid Hydrocarbons

Introduction

The very large reserves of methane, which is the principal component of most natural gas reserves, could serve as a feedstock for the production of chemicals and as a source of energy well into the 21st century. Although methane is currently being used in such important applications such as the heating of homes and the generation of hydrogen for ammonia synthesis, its potential for the production of ethylene or liquid hydrocarbon fuels has not been fully realized.

A number of strategies are being explored at levels that range from fundamental science to engineering technology. However, each alternative has its own set of limitations; for example, in Oxidative Coupling of Methane (OCM), the economical separation of ethylene from dilute product streams is the most important issue. Therefore, a successful methane conversion system that considers catalyst innovations and novel engineering developments is needed to overcome the limitation in the OCM field. As part to discover the solution for this problem, the dual-bed catalytic system has been proposed through the present study. This system comprises of an OCM catalyst, the La-MgO catalyst, while the second bed contains Ni loaded HZSM-5 catalyst.

The primary aims of this paper are to study the performance of the dual-bed catalytic system for direct conversion of methane to liquid hydrocarbons and also to investigate the influence of reaction parameters on the products distribution. Three variables; temperature, CH_4/O_2 ratio and amount of nickel loading on HZSM-5 (%wt), were selected as the independent variables. The optimal range of each factor affecting the yield of C_{5+} hydrocarbons is identified.

Approach and Methods

Catalyst Preparation

La/MgO catalyst was prepared by mixing powdered magnesium oxide (MgO, supplied by GCE with purity >98%) with lanthanum(III) nitrate hexahydrate, $La(NO_3)_3.6H_2O$ (supplied by Merck with purity 99.999%) in deionized water just sufficient to form a thick paste (La/MgO=0.1 ratio). Next, the paste was dried at 120^{0}C drying for 12 hours. The resulting dried mass was then calcined at 800 ^{0}C for 10 hours in static air.

The parent ZSM-5 (SiO_2/Al_2O_3=30) was supplied in the ammonium form by Zeolyst International. To obtain the protonic form, the zeolite was calcined at 500 ^{0}C for 5 hours. The resulting material was then further used for preparing Ni/HZSM-5 catalysts with varied Ni loading according to the wet impregnation method. The samples were prepared by introducing a desired amount of nickel(II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, 98%) aqueous solution into the HZSM-5 zeolite. After the impregnation process, the catalysts were dried at 110 ^{0}C over night and then calcined at 500 ^{0}C for 4 hours. The samples with different Ni loading were denoted as N% Ni/HZSM-5 where N % represents the weight % of Ni introduced.

Catalytic Evaluation

The reaction was performed using a fixed-bed quartz reactor with 10mm inner diameter and 300 mm length at atmospheric pressure. The dual-bed catalystic reactor configurations used in this study are schematically

shown in Figure 1. In the dual-bed catalytic system, the feed gas mixture first passed through the La-MgO catalyst bed and then through the Ni/HZSM-5 catalyst bed. A plug of glass wool separated the two catalyst beds. A Carbolite tube furnace (Model: MTF 0/15/130) was used to heat up the reactor to the required operating temperature. The temperatures reported were those for the OCM bed; the zeolite upper bed (minimum) temperature was measured to be about 115 ^{0}C lower than the OCM bed. This difference of 115 ^{0}C remained constant over the most important range of the OCM bed temperatures, from 650-800 ^{0}C.

For catalyst testing, the catalyst was first activated in situ by heating to 550 ^{0}C for 1 hour in flowing nitrogen before the flow was switched to the reactant gases. The reactant feed gas used in this study were high purity methane (≥99.9% purity) and oxygen (≥99.99%). The inlet volumetric flow rate of each gas was controlled using the individual volumetric flow controller (Alicat) with a flow rate range from 5-512 ml/min. The product stream leaving the reactor was separated into liquid and gas fractions using water bath. The reactor effluent gases were analyzed on-line by means of a Hewlett Packard Agilent 6890N gas chromatograph system equipped with thermal conductivity detector (TCD) and four series column (UCW 982, DC 200, Porapak Q and Molecular Sieve 13A). The fraction of collected liquid products was determined by manually injecting the liquid in the flame ionization detector (FID)-GC. The yield for products were calculated on the carbon basis (coke was not taken into account).

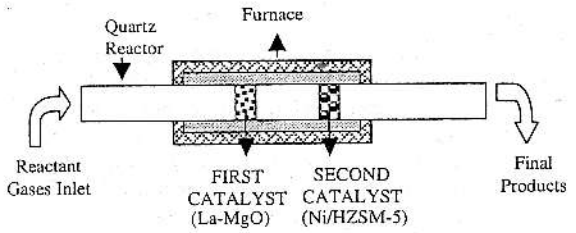

Figure 1: Schematic of dual bed catalysts reactor

Results and Discussions

Effect of Temperature

Figure 2(a) presents the interrelation between the products distribution and the temperature over dual-bed catalytic system in the reaction temperatures between 650 ^{0}C and 800 ^{0}C. All the experiments were conducted using 1% Ni/HZSM-5 as a second bed catalyst and methane to oxygen ratio of 10.

As expected from the kinetic and thermodynamic consideration, high temperature will be advantageous to the methane conversion reaction. Therefore, the conversion of methane is found to increase marginally with increasing reaction temperature. The formation of $CH_3^{\cdot}$ radicals effectively required reaction operation to be at a higher temperature before these radicals undergo coupling reaction in the gas phase to produce ethane. Moreover, the trend for methane conversion for the dual-bed catalytic reactor, observed in this study, is slightly higher compared to the methane conversion profile of single bed La-MgO catalyst as function of temperature which is reported by Choundary *et al.* [1]. The result of this study indicates that methane composition is controlled by the reaction rate on each catalyst and evidently showed that the second bed of Ni/HZSM-5 catalyst also plays a role in the methane transformation.

The C_2H_4/C_2H_6 ratio decreased initially as temperature is increased from 650 ^{0}C to 700 ^{0}C. It is clear that the amount of ethylene in the final product decrease noticeably. It means that at 700 ^{0}C, most of the ethylene efficiently consumed by the second bed Ni/HZSM-5 catalyst. However, further increase of reaction temperature resulted in a visible increase of the C_2H_4/C_2H_6 ratio. There are some possible reasons to clarify this trend. This is expected mostly because of the fact that Ni loaded zeolite catalyst deactivated much more rapidly at higher temperature [2]. Therefore, it is understandable that efficiency of the Ni/HZSM-5 catalyst reduce hastily when temperature increased which sourced more ethylene escaped from additional reaction in second bed catalyst. It can be also due to the non-catalytic (i.e homogeneous) reactions, such as the thermal decomposition of ethyl radicals and thermal cracking of ethane reactions [1], also hoist simultaneously with increase in the rate of oxidative dehydrogenation of ethane both on the catalyst surface and in the gas phase reaction at higher reaction temperatures [3].

It seem that the Bronsted acid sites of HZSM-5 which act as an agent to generate oligomers would easily be victimized at higher temperature and limit the oligomerization reaction [4]. Such a conclusion comes from Figure 2(a), showing that the yield of C_{5+} drop at the higher reaction temperature. Additionally, Sethuraman *et al.* [5] suggested that a decreased selectivity for C_{5+} hydrocarbon formation with increasing temperature might be explained on the basis that an increase in temperature increases the tendency for thermal cracking of any long chain hydrocarbons formed into more stable short chain hydrocarbons.

It is likely that in this temperature regime, the reaction proceeds through a homogenous-heterogenous reaction scheme, with a product distribution that differ signicantly from that observed by using single bed OCM catalyst under the same experimental conditions [1,3]. Considering the above views, we suggest that the role of Ni species on HZSM-5 should not only to simply produce radicals but also to activate a more complex mechanism over its surface.

Effect of Oxygen Concentration

The effect of oxygen concentration in the reactant on the catalysts performances is shown in Figure 2(b) over La-MgO and 1%Ni/HZSM-5 at the reaction temperature of 700 ^{0}C via the dual-bed catalytic system.

In term of catalytic performance, increasing the oxygen concentration was beneficial and boosted methane conversion as a consequent of a decrease in the methane to oxygen ratio. Therefore, considering above consideration and previous reports [6-7], we point out that the methyl radical generation reaction is oxygen concentration dependent. When the CH_4/O_2 ratio is high, more oxygen is available for consuming the methane. Therefore, more oxygen present increases the number and the concentration of the methyl radicals and concurrently increases the conversion of methane as can be observed in Figure 2(b).

Figure 2(b) displays the C_2H_4/C_2H_6 ratio increases when methane to oxygen decreases from 10 to 6. From our point of view, this result exposed that ethane is the initial product and ethylene is subsequently produced by the oxydehydrogenation of ethane to ethylene with increases in oxygen concentration, which fits with the results reported by other investigators [1,3,8]. However, an interesting feature of C_2H_4/C_2H_6 plot this catalytic system is the remarkable decrease in the ratio of C_2H_4 to C_2H_6observed at the high oxygen concentration (CH_4/O_2=4). This corollary indicates that very high oxygen concentration could lower the preferred reaction and be beneficial for the combustion reaction rate. Particularly, we expect that at the high oxygen concentration condition, more excess oxygen in the gas phase origined the combustion of C_2 products mainly ethylene and lowered the quantity of ethylene in the final products.

As pointed out above that the sharp decrease of C_{5+} hydrocarbons is observed at low CH_4/O_2 ratio. These outcomes could be reasonably understood by considering that high oxygen concentration improves the storage of oxygen capacity on the catalysts surface and gas phase. Therefore, the higher combustion rate increases faster than the oligomerization rate at methane to oxygen ratio lower than 8.

This scenario caused combustion and oxidation more preferable at high oxygen concentration in this system. Thus, the variety of final products is determined by competition of combustion and oligomerization reactions at higher oxygen concentration in the second bed catalyst. When the reaction results in Figure 2(b) are viewed in light of the literature and previous studies, one can sees that the ratio of methane to oxygen must be kept at favored value in order to suppress the undesirable homogenous reactions mainly oxidation reaction. The maximum C_{5+} yield achieved from this examination on effect of oxygen concentration is 7.85% (at 29.5% of methane conversion).

Effect of Nickel Loading

Figure 2(c) illustrates the introduction of nickel to the HZSM-5 catalyst had a great impact on the catalytic performance over dual-bed catalytic system. The activities of the unpromoted (0-NZ) and nickel-promoted HZSM-5 catalysts with different amount of nickel content were explored under a constant temperature (700 ^{0}C) and CH_4/O_2 (10:1) ratio.

Based on the methane conversion profile two clear indication can be made. First, undoped HZSM-5 when applied as second bed catalyst showed relatively low activity toward methane molecules compared to nickel loaded HZSM-5. Second, the conversion of methane increases concomitantly with amount of nickel doping. In order to explain this behaviour we confer the results with the surface chemistry of the metal loaded zeolite catalysts. Although in this study does not directly proved the intrinsic connection between surface oxygen and methane conversion. However, some previous studies suggested that there are strong indications that surface oxygen species are responsible for hydrogen abstraction from methane [9]. Therefore, in agreement with previous suggestions, we recommend that by using nickel dopants which have a higher oxygen vacancies are introduced leading to an increase activity compared to unloaded HZSM-5. These centers are proposed to be the active sites for hydrogen abstraction from methane under the formation of a methyl radical. Therefore, the methane conversion profile increases with increase of the amount of nickel loading which used to amend the second bed HZSM-5 catalyst.

Obviously, the metal free catalyst is able to convert ethylene, but much less efficiently than the nickel-containing catalysts. Nevertheless, the activity second bed HZSM-5 catalyst was increased once nickel start introduced. Therefore, a sharp decrease in C_2H_4/C_2H_6 ratio can be viewed in Figure 2(c). This is undoubtedly indicate that nickel species reactive toward olefin mainly ethylene. The ethylene conversion significantly higher for nickel loaded HZSM-5 than for the undoped HZSM-5 catalyst meaning that the consecutive alteration of C_2–products mainly ethylene is cultivated by doping with nickel. However, unclear trend which observed when increase in the amount of nickel loading is hardly predicted. It is because consequently a large number of series of dehydrogenation, hydrogenolysis, cracking and oxidation reactions believed took place which involving C_2 hydrocarbons on the nickel surface.

On the other hand, Espinoze *et al.* [10] proved that the ethylene oligomerization activity of nickel-loaded HZSM-5 catalysts is approximately proportional to the nickel concentration, but with a significant positive bias at the lower nickel contents. Therefore, the yield of C_{5+} products was strongly depending on the nickel concentration. It can observe in Figure 2(c) that 0.5 % nickel loaded HZSM-5 catalyst gave enhanced C_{5+} yield compared to unloaded HZSM-5 catalysts. However, further

decrease in nickel loading caused a decrease in the yield of C_{5+} hydrocarbons.

Three possible hypotheses and explanations are presented for the ascribed profile of C_{5+} yield to support the reasons why high nickel loading of HZSM-5 is not beneficial to oligomerization and cyclization reactions. First, the result of C_{5+} yield viewed in light of some previous characterization results (results not shown) showed that increases in the amount of the nickel loading leads to blockage of the channels and intersections and partially decreases strong acid sites primarily the Bronsted sites. Therefore, this limits the accessibility of intermediate OCM products to undergo further oligomerization and cyclization reaction on Bronsted sites as nickel content increased.

Second hypothesis is probably due to severe coke deposits in the channels of zeolite, as suggested by Tan *et al.* [11]. Generally, the external surface area, accessibility of the zeolite acid sites and its strength played more important roles in determining the amount of coke formation [12]. Likewise, Ermakova *et al.* [13] suggested that remarkably high yield of carbon deposition is due to an increase in the nickel loading causing the catalyst to be easily deactivated. Dong *et al.* [14] as well believed that the nickel loaded HZSM-5 catalyst deactivated rapidly because the size of an average crystallite on the zeolite surface is much larger; this can easily promote the formation of coke. Therefore, the deactivation behavior of catalysts is apparently due to the carbon deposition in the pores of HZSM-5 produced by hydrocarbon decomposition that increase with amount of nickel content forbidding oligomerization and cyclization reactions

Third, doping with nickel ions also caused an increase in the weak acid surface, corresponding with an increase in nickel concentration, where the greater amount of weak acid sites have the opposite effect on the oligomerization reaction [15]. Therefore, the extremely active nickel surface at the high nickel loading caused the partial oxidation and hydrogenolysis become dominant rather than the oligomerization reaction, which caused formation of light hydrocarbons and carbon oxides. On the basis of the available experimental data it is not possible to choose between these possibilities. However, this confirms again that the role of nickel on the second bed should be not only to simply produce radicals but also to activate more complex reactions over its surface.

Some important conclusions can be drawn at this point. The variation of the products described that the complex sets of reactions occurs on the nickel phase involving OCM intermediate products. From the above analysis, it is clear that the increase in methane conversion with increasing amount of nickel doped suggest that the conversion of methane proceeds on the both catalysts. The observations described above strongly suggest that the undesirable effect can be minimized by properly designing the amount of nickel loaded on the HZSM-5 when applied as second bed. A relatively satisfactory result in term of C_{5+} yield was gained over 0.5% Ni/HZSM-5 catalysts compared to unloaded HZSM-5 catalysts. However, if the nickel loading is high enough, the overoxidation of the primary produced olefin and the partial oxidation reaction, clearly favored and these reactions develop as the main reaction compare to the desired oligomerization reaction.

Conclusions

The results of this study demonstrated that the catalytic behavior of a dual-bed system strongly depended on the reaction parameters. It has been observed that the dual-bed catalytic system showed a good activity and yield of higher hydrocarbon products within medium range temperature (c.a. 700^0C). At higher reaction temperatures, dealumination of HZSM-5 became considerable and thus reduced its catalytic performance. Oxygen was absolutely necessary for the formation of the methyl radicals from methane, but it should be provided at a controllable manner in order to avoid undesired oxidation of intermediate OCM products. The rise in oxygen concentration is not beneficial for C_{5+} yield where reaction forming carbon oxides (CO + CO_2) products from combustion of intermediate hydrocarbon products rather than oligomerization reaction is dominant. The observations described above strongly suggest that the undesirable effect can be minimized by properly designing the amount of nickel loaded on the HZSM-5 when applied as second bed.

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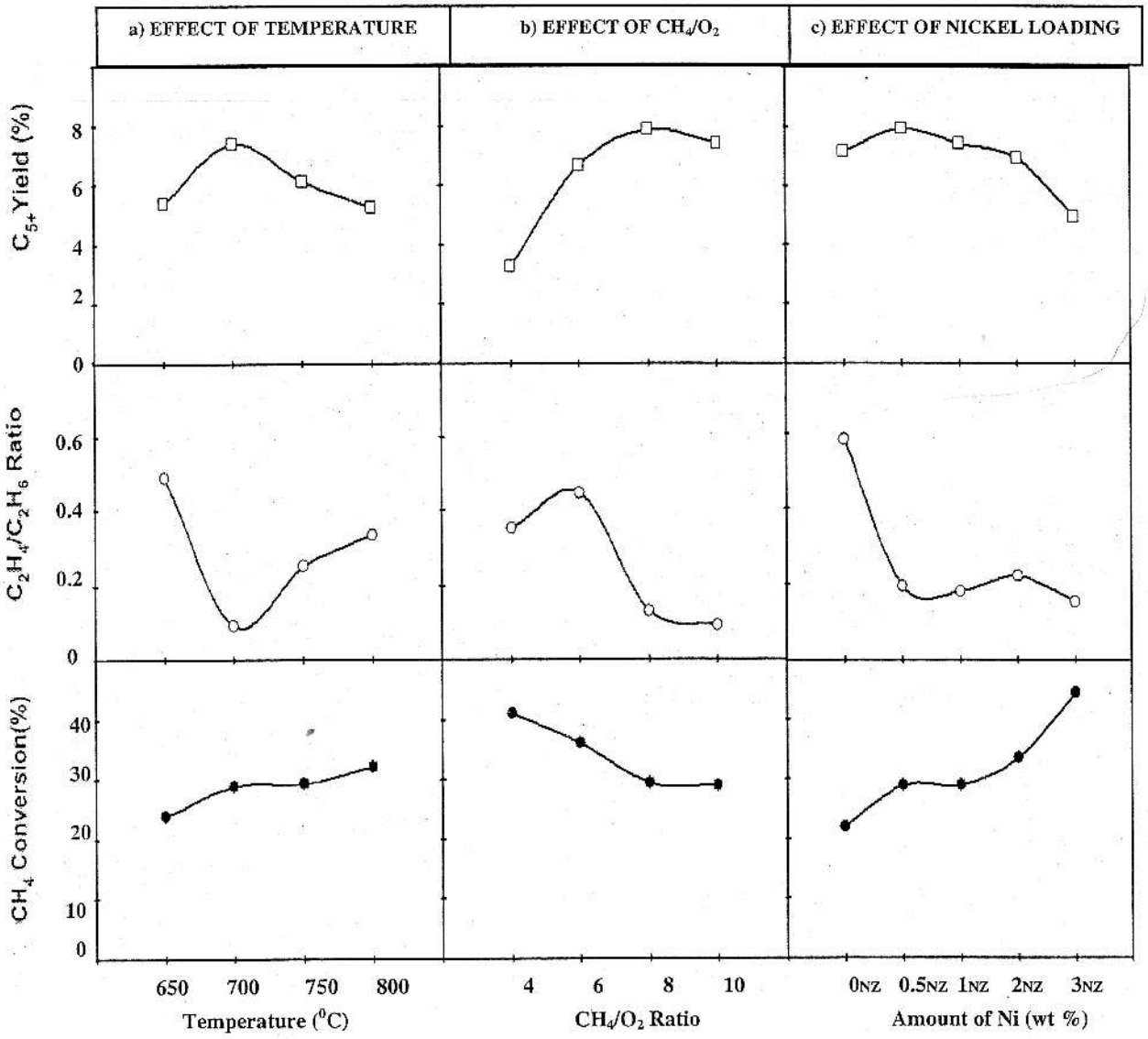

Figure 2: Influence of reaction parameters on the catalytic activity and products distribution (• methane conversion, ○ ethylene to ethane ratio and □ yield of C_{5+})